THE STATISTICAL THEORY OF SPONTANEOUS FLUCTUATIONS IN ENERGY, PRESSURE, AND DENSITY.

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Abstract.

Theoretical derivation of expressions for fluctuations in energy, pressure, and density.—The fluctuation of a quantity, such as the energy, is defined as the ratio of the average deviation from the mean energy to the mean energy. The following expressions are deduced from a new statistical theory for ordinary temperature and pressure: Fluctuation in energy at constant volume $= \sqrt{(2/\gamma n f)}$ and at constant temperature $= 2/f\sqrt{n}$; Fluctuation in pressure or density at constant temperature $= 1/\sqrt{n}$; where n is the number of molecules, f the number of degrees of freedom of each, and γ the ratio of total energy to kinetic energy. At the critical condition the first of these becomes $(12/\gamma n f)^{1/4}$ and the last $(6/n)^{1/4}$. The expressions obtained by Smoluchowski, Hauer, Fürth and Laue are shown to be special cases of the above. Relations are obtained between the various types of fluctuations for the case of an ideal gas.

Introduction.

In 1904 Smoluchowski[1] obtained from theoretical considerations the equation for the mean isothermal fluctuation of density of a gas $|\bar{\delta}_e|_T$ due to molecular collisions

$$|\bar{\delta}_e|_T = \sqrt{\frac{2}{\pi n}} = \frac{.797}{\sqrt{n}}, \tag{1}$$

where n is the number of molecules inside the volume considered.

This equation being true for a gas will also hold for colloidal particles. As a result of a series of observations[2] with colloidal solutions Svedberg, Westgren and others found that the fluctuation of density really obeys Smoluchowski's equation.

In 1908 Smoluchowski[3] showed that at the critical condition of a gas $|\bar{\delta}_e|_T$ is given by the equation

$$|\bar{\delta}_e|_T = \frac{1.13}{\sqrt[4]{n}}, \tag{2}$$

which was subsequently verified by Kammarlingh Onnes and Keesom.[4] Thus at the critical state the mean fluctuation is greater than at the ordinary condition. Smoluchowski, however, suggested that this fluc-

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[1] Boltzman, Festschrift, s. 626 (1904).

[2] Svedberg, Die Existenz der Moleküle, Leipzig, 1912.

[3] Ann. d. Phys., 25, 205 (1908).

[4] Comm. fr. the Phys. Lab. of Leiden (1908).

tuation of density might give rise to opalescence noticeable at the critical state of a gas. But he did not in that paper obtain any expression for the intensity of the opalescent light. Subsequently in 1910 Einstein [1] obtained the value of the mean intensity of opalescent light which agreed with Keesom's [2] equation found experimentally on working with ethylene at its critical condition. It is noteworthy that in deducing the equation Einstein supposed the variation of density to be a circular function of the coördinates. Now the intensity of opalescent light [3] as calculated from Smoluchowski's equation is exactly the same as that from Einstein's equation putting $\phi = 0$. This is again an indirect verification of Smoluchowski's equation (2).

Later in 1915 F. v. Hauer [4] obtained an expression for the isochoric temperature fluctuation of an ideal gas at the ordinary conditions.

$$(\overline{\delta_T^2})_v = 2/3n. \tag{3}$$

More recently, however, M. v. Laue [5] and R. Fürth [6] have found the energy and pressure fluctuations by a somewhat similar method.

$$\overline{\delta_u^2} = \frac{KT_0v_0}{\Delta v\cdot\overline{U}^2}\left\{-\frac{(d\overline{U}/dv)^2}{(dp/dv)} + C_vT_0\right\} \qquad \text{(Laue)}, \tag{4}$$

$$\overline{\delta_p^2} = x/n \quad \text{where} \quad x = C_p/C_v \qquad \text{(Fürth)}. \tag{5}$$

It should be noted, however, that in these two kinds of fluctuations the temperature and volume are not constant.

In the present paper it is proposed to develop a statistical theory of the different kinds of fluctuations.

Statistical Theory.

Let us consider a volume containing n molecules within a large volume of a gas and suppose each molecule has f degrees of freedom. Then the behavior of the gas in the volume considered is given at any instant by the position of the representative point in $2nf$ dimensional phase space. Now due to molecular collisions and other factors, the representative point does not move in the same energy surface U_0 but between two energy surfaces U_0 and $U_0 + dU_0$. Or in other words the representative points are canonically distributed in Gibbs's phase space according to

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[1] Ann. d. Phys., 33, 1294 (1910).

[2] Ann. d. Phys., 35, 591 (1911).

[3] Die Theorie der Strahlung und der Quanten, von A. Eucken, p. 182, W. Knapp (1914).

[4] Hauer, Ann. der Phys. 47, 365, 1915.

[5] Laue, Phys. Zeit. 18, 542, 1917; also R. Fürth, Schwankungserscheinungen in der Physik.

[6] Fürth, Phys. Zeit. 20, 350, 1919.

the equation[1]

$$\epsilon = Ne^{\frac{\psi - U}{\theta}},$$

where U is the energy.

Thus in the canonical distribution the energy of the representative point does not remain constant but fluctuates within a certain range. And this fluctuation of energy, or the "dispersion of energy" as it is generally called, of the representative point measures the variation of energy of the n molecules which it represents. If we suppose the potential energy of the molecules to be nothing, the fluctuation of energy of the molecules can be caused only by the dispersion in the velocity or the positional space. Thus the total dispersion of energy is equal to the sum of the two partial dispersions in the velocity and the positional space. And it is evident that the energy fluctuation, when there is no dispersion in the positional space (Lagenraum), will correspond to the energy or temperature fluctuation at constant volume (Hauer). Then again the fluctuation of energy at constant velocity space will give rise to pressure fluctuation at constant temperature. But they will not be identical as will be discussed below. Now let us calculate the energy or the temperature fluctuation at constant volume from the dispersion theory.

We have for the fluctuation of energy, $(U - \overline{U})/\overline{U}$.

Suppose

$$U = \overline{U} + \xi;$$

therefore

$$U^2 = (\overline{U})^2 + \xi^2 + 2\xi \cdot \overline{U}.$$

Taking the mean and remembering that $\overline{\xi} = 0$ we have

$$\overline{\xi^2} = \overline{U^2} - (\overline{U})^2;$$

therefore

$$\overline{\delta}_u{}^2 = \frac{\overline{U^2} - (\overline{U})^2}{(\overline{U})^2}.$$

Also:

$$\overline{U} = \frac{\int U e^{-\frac{U}{\theta}} \Delta\tau}{\int e^{-\frac{U}{\theta}} \Delta\tau},$$

$$\overline{U^2} = \frac{\int U^2 e^{-\frac{U}{\theta}} \Delta\tau}{\int e^{-\frac{U}{\theta}} \Delta\tau},$$

where $\Delta\tau = \Delta\tau_p \cdot \Delta\tau_q$.

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[1] C. Shaefer, Einführung in die theoretische Physik, Bd. II., Berlin, 1921; also Gibbs, Statistical Mechanics.

(6) Putting x for $1/\theta$ and P for $\int e^{-\frac{U}{\theta}}\Delta\tau$ or $\int e^{-Ux}\Delta\tau$, we have

$$\bar{U} = -\frac{1}{P}\frac{dP}{dx}, \tag{7}$$

$$\overline{U^2} = \frac{1}{P}\frac{d^2P}{dx^2}. \tag{8}$$

Therefore

$$\overline{\xi^2} = \overline{U^2} - (\bar{U})^2 = \frac{1}{P}\frac{d^2P}{dx^2} - \frac{1}{P^2}\left(\frac{dP}{dx}\right)^2$$
$$= \frac{d}{dx}\left(\frac{\frac{dP}{dx}}{P}\right).$$

Hence remembering (7)

$$\overline{\xi^2} = -\frac{d\bar{U}}{dx}$$
$$= \theta^2\frac{d\bar{U}}{d\theta} \text{ from (6).}$$

Suppose $\bar{U} = \gamma\bar{L}$,[1] $\bar{L}$ being the kinetic energy. From the equipartition theorem

$$\bar{U} = \frac{\gamma n f}{2}\theta, \tag{9}$$

so that

$$\overline{\xi^2} = \frac{\gamma n f}{2}\theta^2.$$

Hence

$$(\overline{\delta_u^2})_v = \frac{2}{\gamma n f}$$

or

$$|\bar{\delta}_u|_v = \sqrt{\frac{2}{\gamma n f}}.$$

For ideal gas or colloidal particles $\gamma = 1$ and $f = 3$, thus, at ordinary temperature and pressure,

$$|\bar{\delta}| = \sqrt{\frac{2}{3n}} = \frac{.816}{\sqrt{n}},$$

which is Hauer's equation.

At the critical condition we suppose $\overline{\xi^2} = 0$, so

$$\overline{\delta_u^4} = \frac{\overline{\xi^4}}{(\bar{U})^4} = \frac{\overline{U^4} - (\bar{U})^4}{(\bar{U})^4}. \tag{10}$$

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[1] For an ideal gas, the potential energy $\bar{\phi}$ is zero, so that $\gamma = 1$, but for solids $\bar{\phi} = \bar{L}$, *i.e.*, $\gamma = 2$.

Differentiating (7) with respect to x we have

$$\frac{d}{dx}(\overline{U}) = \frac{-\dfrac{d^2P}{dx^2}}{P} + \frac{\left(\dfrac{dP}{dx}\right)^2}{P^2}\,. \tag{11}$$

On further differentiation with respect to x

$$\frac{d^2}{dx^2}(\overline{U}) = \frac{-\dfrac{d^3P}{dx^3}}{P} + \frac{3\dfrac{dP}{dx}\cdot\dfrac{d^2P}{dx^2}}{P^2} - \frac{2\left(\dfrac{dP}{dx}\right)^3}{P^3}\,. \tag{12}$$

On differentiating again

$$\frac{d^3}{dx^3}(\overline{U}) = \frac{-\dfrac{d^4P}{dx^4}}{P} + 4\cdot\frac{\dfrac{d^3P}{dx^3}\cdot\dfrac{dP}{dx}}{P^2} + 3\frac{\left(\dfrac{d^2P}{dx^2}\right)^2}{P^2} - 12\frac{\left(\dfrac{dP}{dx}\right)^2\dfrac{d^2P}{dx^2}}{P^3} + 6\frac{\left(\dfrac{dP}{dx}\right)^4}{P^4}\,. \tag{13}$$

Substituting the value of $\overline{U}$ from (9) in (11) remembering (8)

$$\begin{aligned} \overline{U^2} &= \theta^2\frac{d\overline{U}}{d\theta} + (\overline{U})^2 \\ &= \frac{\theta^2\gamma nf}{2}\left(1 + \frac{\gamma nf}{2}\right). \end{aligned} \tag{11a}$$

Again substituting values of $\overline{U^2}$ and $\overline{U}$ in (12) we have

$$\begin{aligned} -\overline{U^3} &= -\theta^3\gamma nf + \frac{3}{4}\theta^3\gamma^2n^2f^2\left(1 + \frac{\gamma nf}{2}\right) - \frac{\gamma^3n^3f^3\theta^3}{4} \\ &= \theta^3\gamma nf\left\{-1 + \frac{3}{4}\gamma nf\left(1 + \frac{\gamma nf}{2}\right) - \frac{\gamma^2n^2f^2}{4}\right\}. \end{aligned} \tag{12a}$$

Similarly from (13)

$$\begin{aligned} \overline{U^4} = {} & 3\theta^4\gamma nf + 2\gamma nf\theta\cdot\theta^3\gamma nf\left\{-1 + \frac{3}{4}\gamma nf\left(1 + \frac{\gamma nf}{2}\right) - \frac{\gamma^2n^2f^2}{4}\right\} \\ & + 3\cdot\frac{\theta^4\gamma^2n^2f^2}{4}\left(1 + \frac{\gamma nf}{2}\right)^2 \\ & - 12\cdot\frac{\theta^2\gamma^2n^2f^2}{4}\cdot\frac{\theta^2\gamma nf}{2}\left(1 + \frac{\gamma nf}{2}\right) + 6\frac{\gamma^4n^4f^4\theta^4}{16}\,. \end{aligned} \tag{13a}$$

Therefore

$$\overline{\xi^4} = \overline{U^4} - (\overline{U})^4 = 3\theta^4\gamma nf + 2\theta^4\gamma^2n^2f^2\left\{-1 + \frac{3}{4}\gamma nf\left(1 + \frac{\gamma nf}{2}\right) - \frac{\gamma^2n^2f^2}{4}\right\}$$

$$+ 3\cdot\frac{\theta^4\gamma^2n^2f^2}{4}\left(1 + \frac{\gamma nf}{2}\right)^2 - 12\frac{\theta^4\gamma^3n^3f^3}{8}\left(1 + \frac{\gamma nf}{2}\right) + 5\cdot\frac{\gamma^4n^4f^4\theta^4}{16}$$

$$= \frac{3}{4}\gamma^3 n^3 f^3 \theta^4 - \frac{5}{4}\gamma^2 n^2 f^2 \theta^4 + 3\gamma n f \theta^4.$$

Hence

$$(\overline{\delta_u^4})_v = \frac{\frac{3}{4}\gamma^3 n^3 f^3 \theta^4 - \frac{5}{4}\gamma^2 n^2 f^2 \theta^4 + 3\gamma n f \theta^4}{\frac{1}{16}\gamma^4 n^4 f^4 \theta^4}$$

$$= \frac{12}{\gamma n f} - \frac{20}{\gamma^2 n^2 f^2} + \frac{48}{\gamma^3 n^3 f^3}$$

$$= \frac{12}{\gamma n f}$$

when n is large or

$$|\bar{\delta}_u|_v = \sqrt[4]{\frac{12}{\gamma n f}}\,.$$

For simplicity we suppose $\phi = 0$ or $\gamma = 1$, so that

$$|\bar{\delta}_u|_v = \sqrt[4]{\frac{12}{nf}}\,. \tag{14}$$

Let us now find the pressure fluctuation at constant temperature. As before we have the isothermal pressure fluctuation at ordinary conditions given by

$$(\overline{\delta_p^2})_T = \frac{\overline{p^2} - (\bar{p})^2}{(\bar{p})^2}\,. \tag{15}$$

Also:

$$\bar{p} = \frac{\int (dU/dv) e^{-U/\theta} \Delta\tau}{\int e^{-U/\theta} \Delta\tau},^{1}$$

$$\overline{p^2} = \frac{\int (dU/dv)^2 e^{-U/\theta} \Delta\tau}{\int e^{-U/\theta} \Delta\tau}\,.$$

Remembering (6) we have

$$\frac{dP}{dv} = -\frac{1}{\theta}\int \frac{dU}{dv} e^{-U/\theta} \Delta\tau,$$

$$\frac{d^2P}{dv^2} = +\frac{1}{\theta^2}\int \left(\frac{dU}{dv}\right)^2 e^{-U/\theta} \Delta\tau.$$

Hence we have

$$\begin{aligned} \bar{p} &= -\theta \frac{dP/dv}{P}, \\ \overline{p^2} &= +\theta^2 \frac{d^2P/dv^2}{P}\,. \end{aligned} \tag{16}$$

Substituting (16) in (15) and after transformation we get

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[1] C. Schaefer, loc. cit., p. 445 (85).

(17) $$(\overline{\delta_p^{\,2}})_T = \theta^2 \frac{d}{dv}\left(\frac{dP/dv}{P}\right)\Big/(\bar{p})^2 = -\,\theta\frac{d\bar{p}/dv}{(\bar{p})^2}\,;$$

(18) but $\bar{p} = n\theta/v$.[1]

Using (18) we get

(19) $$(\overline{\delta_p^{\,2}})_T = 1/n.$$

Now at the critical condition, dp/dv in (17) is zero, so that $(\overline{\delta_p^{\,2}})_T = 0$. Therefore the critical fluctuation of pressure will be given by

(20) $$(\overline{\delta_p^{\,4}})_T = \frac{\overline{p^4} - (\bar{p})^4}{(\bar{p})^4}\,.$$

The right-hand term of equation (20) is evaluated as in (10) and we have

$$(\overline{\delta_p^{\,4}})_T = \frac{6}{n} + \frac{11}{n^2} + \frac{6}{n^3}\,,$$

or when n is large

(21) $$(\overline{\delta_p^{\,4}})_T = 6/n, \quad \text{i.e. } |\bar{\delta}_p|_T = 1\cdot 56/\sqrt[4]{n}.$$

One may note here that the iosthermal energy fluctuation cannot be obtained as the isothermal pressure fluctuation. Therefore a special device has been used in this case. It is not difficult to see that equation (17), in which p is taken only as a function of volume, is perfectly general and it will be possible to get the value of $(\overline{\delta_u^{\,2}})_T$ by simply putting U for p. We thus have from (17)

$$(\overline{\delta_u^{\,2}})_T = -\,\theta\frac{d\bar{U}}{dv}\Big/(\bar{U})^2 = -\,\theta\frac{\bar{p}}{(\bar{U})^2}\,.$$

Now remembering $\bar{U} = (f/2)(n\theta/v)$ and $\bar{p} = n\theta/v$, we have

(22) $$(\overline{\delta_u^{\,2}})_T = 4/f^2 n.$$

We leave the matter here to discuss it later on in connection with Laue's energy fluctuation.

Relation Between Different Kinds of Fluctuation.

After deducing from the dispersion theory the values of $(\overline{\delta_u^{\,2}})_v$, $(\overline{\delta_T^{\,2}})_v$, $(\overline{\delta_u^{\,2}})_T$ and $(\overline{\delta_p^{\,2}})_T$, we shall next proceed to find the different kinds of fluctuations considered by previous workers referred to in the introduction, from the fundamental relation proved just now.

From the gas equation $pv = RT$ we have

$$(p^2 + \overline{\Delta p^2})\,(v^2 - \overline{\Delta v^2}) = R^2(T^2 + \overline{\Delta T^2}),$$

where the bar represents the mean fluctuation of the corresponding quantities.

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[1] C. Schaefer, loc. cit., p. 447 (98).

(23) Hence $$\frac{\overline{\Delta p^2}}{p^2} - \frac{\overline{\Delta v^2}}{v^2} = \frac{\overline{\Delta T^2}}{T^2}\,.$$

From the above equation we get the following fundamental relations:

(24a) $$(\overline{\delta_p^2})_T = (\overline{\delta_v^2})_T,$$

(24b) $$(\overline{\delta_p^2})_v = (\overline{\delta_T^2})_v,$$

(24c) $$(\overline{\delta_v^2})_p = -\,(\overline{\delta_T^2})_p,$$

(24d) $$\overline{\delta_v^2} = \bar{\delta}_\rho^2,$$

where ρ is the density.

Now combining (24a) and (24d) we have

$$(\overline{\delta_p^2})_T = (\overline{\delta_\rho^2})_T$$

and hence with the help of (19) we have

(25) $$(\overline{\delta_\rho^2})_T = 1/n,$$

which is Smoluchowski's density fluctuation.[1]

Again we have the general equation

$$\overline{\delta_p^2} = (\overline{\delta_p^2})_T + (\overline{\delta_p^2})_v.$$

Now using (24b) we have

$$\overline{\delta_p^2} = (\overline{\delta_p^2})_T + (\overline{\delta_T^2})_v = (\overline{\delta_p^2})_T + (\overline{\delta_u^2})_v,$$

or substituting the values of terms in the right-hand side of the equation we get

$$\begin{aligned} \overline{\delta_p^2} &= 1/n + 2/fn \\ &= x/n \quad \text{where} \quad x = (f+2)/f, \end{aligned}$$

and this is Fürth's equation (5) for pressure fluctuation at the ordinary conditions. And at the critical state this fluctuation will be $6x/n$ as will be seen from (14) and (21).

Similarly we have for the energy fluctuation

$$\begin{aligned} \overline{\delta_u^2} &= (\overline{\delta_u^2})_v + (\overline{\delta_u^2}). \\ &= 2/fn + 4/f^2n = 2x/fn, \end{aligned}$$

this being Laue's equation as will be seen by transforming his original equation (4) with the help of the well-known formulæ

$$\frac{d\overline{U}}{dv} = \overline{p} = \frac{nkT}{v}, \quad \text{where} \quad kT = \theta,$$

$$\overline{U} = (f/2)(nkT/v) \quad \text{and} \quad c_v = (f/2)(nk/v).$$

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CALCUTTA, March 29, 1923.

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[1] In his paper referred to in the introduction, Smoluchowski has calculated $|\bar{\delta}_\rho|_T$ and not $(\overline{\delta_\rho^2})_T$. But $(\overline{\delta_\rho^2})_T$ calculated from his theory is exactly as in (25). See Fürth, Schwankungserscheinungen, pp. 22 and 55.